

CLAIMS

What is claimed is:

1. A curable, water-based coating composition comprising the reaction product of:

5 (A) a water-based copolymer prepared by free-radical polymerization, said copolymer comprising the reaction product of;

525/92K  
524/505  
(I) a first block comprising the reaction product of;

(a) at least one ethylenically unsaturated monomer, and

(b) at least one vinylaromatic hydrocarbon monomer; and

10 (II) a second block comprising the reaction product of;

(a) a plurality of ethylenically unsaturated monomers different than (A)(I)(a), wherein at least one of said plurality includes at least one carbonate functional group for modification into a carbamate functional group; and

(B) at least one cross-linking agent reactive with said carbamate functional group and dispersible in water.

15 2. A coating composition as set forth in claim 1 wherein said at least one cross-linking agent (B) is selected from the group consisting of water-dispersible aminoplasts, water-dispersible polymers having acrylamide groups, and water-dispersible polymers having methylol or alkoxymethyl groups, and mixtures thereof.

20 3. A coating composition as set forth in claim 2 wherein said water-dispersible aminoplasts are selected from the group of melamine formaldehyde resins having a methylol group, an alkoxymethyl group, or both, which are reactive with said carbamate functional group.

4. A coating composition as set forth in claim 1 further including an ammonia-containing compound reactive with said ethylenically unsaturated monomer of said plurality (A)(II)(a) that includes said carbonate functional group, said ammonia containing compound modifying said carbonate functional group into said carbamate functional group.

5. A coating composition as set forth in claim 4 wherein said ethylenically unsaturated monomer of said plurality (A)(II)(a) that includes said carbonate functional group is selected from the group consisting of carbonate-modified glycidyl acrylate, carbonate-modified glycidyl methacrylate, and mixtures thereof.

6. A coating composition as set forth in claim 4 wherein said ammonia-containing compound is selected from the group consisting of ammonia, ammonium hydroxide, and mixtures thereof.

7. A coating composition as set forth in claim 1 wherein said first block (A)(I) is present in an amount from 5 to 15 parts by weight based on 100 parts by weight of said coating composition.

8. A coating composition as set forth in claim 1 wherein said second block (A)(II) is present in an amount from 25 to 50 parts by weight based on 100 parts by weight of said coating composition.

9. A coating composition as set forth in claim 1 wherein said at least one cross-linking agent is present in an amount from 0.1 to 10 parts by weight based on 100 parts by weight of said coating composition.

10. A coating composition as set forth in claim 1 wherein said first block (A)(I) further comprises the reaction product of a neutralizing agent.

11. A coating composition as set forth in claim 10 wherein said neutralizing agent is selected from the group consisting of dimethylethanolamine, amino methyl propanol, ammonia, and mixtures thereof.

12. A coating composition as set forth in claim 1 wherein said first block  
5 (A)(I) further comprises the reaction product of an initiator.

13. A coating composition as set forth in claim 12 wherein said initiator is selected from the group consisting of inorganic persulfates, dialkyl peroxides, hydroperoxides, peresters, and mixtures thereof.

14. A coating composition as set forth in claim 12 wherein the weight ratio of  
10 said initiator to said at least one vinylaromatic hydrocarbon monomer (A)(I)(b) is from 1 : 3 to 3 : 1.

15. A coating composition as set forth in claim 1 wherein said at least one ethylenically unsaturated monomer (A)(I)(a) is further defined as a first and second ethylenically unsaturated monomer.

16. A coating composition as set forth in claim 15 wherein said first  
15 ethylenically unsaturated monomer is acrylic acid.

17. A coating composition as set forth in claim 16 wherein said second ethylenically unsaturated monomer is methyl methacrylate.

18. A coating composition as set forth in claim 15 wherein said first  
20 ethylenically unsaturated monomer is selected from the group of compounds consisting of alkyl acrylic acids, and said second ethylenically unsaturated monomer is selected from the group of compounds consisting of aliphatic acrylates, aliphatic methacrylates, cycloaliphatic acrylates, cycloaliphatic methacrylates, and mixtures thereof, wherein each

of said first and second ethylenically unsaturated monomers include up to 20 carbon atoms in the alkyl radical.

19. A coating composition as set forth in claim 18 wherein the weight ratio of said first ethylenically unsaturated monomer to said second ethylenically unsaturated monomer is from 1 : 0.5 to 1 : 5.

20. A coating composition as set forth in claim 1 wherein said at least one ethylenically unsaturated monomer (A)(I)(a) is selected from the group of compounds consisting of aliphatic acrylates, aliphatic methacrylates, cycloaliphatic acrylates, cycloaliphatic methacrylates, alkyl acrylic acids, and mixtures thereof, each of said compounds having up to 20 carbon atoms in the alkyl radical.

21. A coating composition as set forth in claim 20 wherein said aliphatic acrylates are selected from the group consisting of methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, hexyl acrylate, ethylhexyl acrylate, stearyl acrylate, lauryl acrylate, and mixtures thereof.

22. A coating composition as set forth in claim 20 wherein said aliphatic methacrylates are selected from the group consisting of methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, hexyl methacrylate, ethylhexyl methacrylate, stearyl methacrylate, lauryl methacrylate, and mixtures thereof.

23. A coating composition as set forth in claim 20 wherein said cycloaliphatic acrylate is further defined as cyclohexyl acrylate.

24. A coating composition as set forth in claim 20 wherein said cycloaliphatic methacrylate is further defined as cyclohexyl methacrylate.

25. A coating composition as set forth in claim 20 wherein said alkyl acrylic acids are selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, and mixtures thereof.

26. A coating composition as set forth in claim 1 wherein said at least one vinylaromatic hydrocarbon monomer (A)(I)(b) is selected from the group consisting of  $\alpha$ -methylstyrene, diphenylethylene, dinaphthaleneethylene, and mixtures thereof.

27. A coating composition as set forth in claim 1 wherein said plurality of ethylenically unsaturated monomers (A)(II)(a) are selected from the group consisting of styrene, butyl acrylate, butyl methacrylate, 2-ethylhexyl methacrylate, 2-hydroxyethyl methacrylate, cyclohexyl methacrylate, glycidyl acrylate, glycidyl methacrylate, carbonate-modified glycidyl acrylate, carbonate-modified glycidyl methacrylate, and mixtures thereof, such that said plurality of ethylenically unsaturated monomers (A)(II)(a) are different than (A)(I)(a) and at least one of said plurality (A)(II)(a) includes said carbonate functional group.

28. A coating composition as set forth in claim 1 further comprising the reaction product of an anionic surfactant.

29. A coating composition as set forth in claim 1 wherein said first block (A)(I) has a molecular weight of from 1,000 to 20,000.

30. A coating composition as set forth in claim 1 having a non-volatile content of from 20 to 60 percent non-volatile by weight.

31. A coating composition as set forth in claim 1 having an average particle size of less than or equal to 200 nm.

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33. A method of preparing a curable, water-based coating composition, said method comprising the steps of:

(A) forming a first block;

(B) polymerizing a second block having at least one carbonate functional

5 group with the first block to establish a water-based copolymer;

(C) converting the at least one carbonate functional group in the second block of the water-based copolymer into at least one carbamate functional group; and

(D) combining the water-based copolymer with at least one cross-linking agent that is reactive with the carbamate functional group and dispersible in water.

10 34. A method as set forth in claim 33 wherein the at least one cross-linking agent (B) is selected from the group consisting of water-dispersible aminoplasts, water-dispersible polymers having acrylamide groups, and water-dispersible polymers having methylol or alkoxymethyl groups, and mixtures thereof.

15 35. A method as set forth in claim 34 wherein the water-dispersible aminoplasts are selected from the group of melamine formaldehyde resins having a methylol group, an alkoxymethyl group, or both, which are reactive with the carbamate functional group.

20 36. A method as set forth in claim 33 wherein the step of (C) converting the at least one carbonate functional group in the second block of the water-based copolymer into the at least one carbamate functional group is further defined as reacting an ammonia-containing compound selected from the group consisting of ammonia, ammonium hydroxide, and mixtures thereof, with the carbonate functional group to convert the carbonate functional group into the carbamate functional group.

37. A method as set forth in claim 33 wherein the steps of (A) - (C) are conducted at a temperature between 50°C and 100°C.

38. A method as set forth in claim 33 wherein the step of (A) forming the first block is further defined as polymerizing at least one ethylenically unsaturated monomer and at least one vinylaromatic hydrocarbon monomer to form the first block of the water-based copolymer.

39. A method as set forth in claim 38 wherein the step of polymerizing the at least one ethylenically unsaturated monomer and the at least one vinylaromatic hydrocarbon monomer is conducted over time from 1 to 8 hours.

40. A method as set forth in claim 38 wherein the step of (A) forming the first block further includes the step of adding a neutralizing agent selected from the group consisting of dimethylethanolamine, amino methyl propanol, ammonia, and mixtures thereof, to the at least one ethylenically unsaturated monomer and the at least one vinylaromatic hydrocarbon monomer to form the first block of the water-based copolymer.

41. A method as set forth in claim 38 wherein the step of (A) forming the first block further includes the step of adding an initiator selected from the group consisting of inorganic persulfates, dialkyl peroxides, hydroperoxides, peresters, and mixtures thereof, to the at least one ethylenically unsaturated monomer and the at least one vinylaromatic hydrocarbon monomer to form the first block of the water-based copolymer.

42. A method as set forth in claim 38 wherein the at least one ethylenically unsaturated monomer is selected from the group of compounds consisting of aliphatic acrylates, aliphatic methacrylates, cycloaliphatic acrylates, cycloaliphatic methacrylates,



alkyl acrylic acids, and mixtures thereof, each of the compounds having up to 20 carbon atoms in the alkyl radical.

43. A method as set forth in claim 38 wherein the at least vinyl aromatic hydrocarbon monomer is selected from the group consisting of  $\alpha$ -methylstyrene, diphenylethylene, dinaphthaleneethylene, and mixtures thereof.

44. A method as set forth in claim 33 wherein the step of (B) polymerizing the second block having at least one carbonate functional group with the first block is further defined as polymerizing a plurality of ethylenically unsaturated monomers with the first block, wherein at least one of the plurality includes the carbonate functional group that is converted into the carbamate functional group, to form the second block of the water-based copolymer.

45. A method as set forth in claim 44 wherein the step of polymerizing the plurality of ethylenically unsaturated monomers with the first block is conducted over time from 1 to 8 hours.

46. A method as set forth in claim 44 wherein the plurality of ethylenically unsaturated monomers are selected from the group consisting of styrene, butyl acrylate, butyl methacrylate, 2-ethylhexyl methacrylate, 2-hydroxyethyl methacrylate, cyclohexyl methacrylate, glycidyl acrylate, glycidyl methacrylate, carbonate-modified glycidyl acrylate, carbonate-modified glycidyl methacrylate, and mixtures thereof, such that at least one of the plurality includes the carbonate functional group.

47. A method as set forth in claim 34 wherein the step of (D) combining the water-based copolymer with the at least one cross-linking agent further includes the step

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50 A method of preparing a cured film of a water-based coating composition, said method comprising the steps of:

(A) forming a first block;

(B) polymerizing a second block having at least one carbonate functional group with the first block to establish a water-based copolymer;

(C) converting the at least one carbonate functional group in the second block of the water-based copolymer into at least one carbamate functional group; and

(D) combining the water-based copolymer with at least one cross-linking agent that is dispersible in water and reactive with the carbamate functional group to form the water-based coating composition;

(E) applying the water-based coating composition to a substrate; and

(F) curing the water-based coating composition to form the cured film.

51. A method as set forth in claim 50 wherein the step of (E) applying the water-based coating composition to the substrate is further defined as spraying the water-based coating composition on to the substrate.

52. A method as set forth in claim 50 wherein the step of (F) curing the water-based coating composition is further defined as reacting the cross-linking agent with the at least one carbamate functional group to form the cured film of the water-based coating composition.

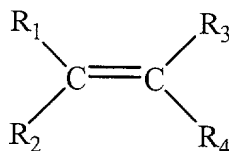
53. A method as set forth in claim 52 wherein the cross-linking agent is a water-dispersible aminoplast selected from the group of melamine formaldehyde resins having a methylol group, an alkoxymethyl group, or both, which are reactive with the carbamate functional group.

5 55. A method as set forth in claim 52 wherein the step of reacting the cross-linking agent with the at least one carbamate functional group is conducted at a temperature between 100°C and 175°C.

56. A curable, water-based coating composition comprising the reaction product of:

(A) a water-based copolymer prepared by free-radical polymerization, said copolymer comprising the reaction product of;

- 5 (I) a first block comprising the reaction product of;
- (a) at least one ethylenically unsaturated monomer, and
  - (b) at least one ethylenically unsaturated monomer different than (A)(I)(a) and of the general formula



10 wherein the radicals each independently of one another are hydrogen atoms or substituted or unsubstituted alkyl, cycloalkyl, alkylcycloalkyl, cycloalkylalkyl, aryl, alkylaryl, cycloalkylaryl, arylalkyl or arylcycloalkyl radicals, with the proviso that at least two of the variables  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are substituted or unsubstituted aryl, arylalkyl or arylcycloalkyl radicals, especially substituted or unsubstituted aryl radicals; and

- 15 (II) a second block comprising the reaction product of;
- (a) a plurality of ethylenically unsaturated monomers different than (A)(I)(a) and (A)(I)(b), wherein at least one of said plurality includes at least one
- 20 carbonate functional group for modification into a carbamate functional group; and

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